THE STRUCTURES OF THE IONIC CRYSTALS BROOKITE AND COLUMBITE

Thesis by

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For encouragement, advice, and direction in the course of the studies here reported, the author is grateful to Professor Linus Pauling.

XV. The crystal structure of brookite.

By

Linus Pauling and J. H. Sturdivant in Pasadena.

(With 6 figures.)

I. Introduction.

In the study of the structure of a crystal with X-rays the effort has been made by many workers, especially Wyckoff and Dickinson in America, to eliminate rigorously all but one of the possible atomic arrangements consistent with the smallest unit of structure permitted by the experimental data, without reference to whether or not the arrangements were chemically reasonable or were in accord with assumed interatomic distances. The importance of this procedure arises from the certainty with which its results can be accepted. For although structure determinations by less rigorous methods have been found to be false, no important error has yet been detected in any investigation which interpreted photographic data solely with space-group theory aided by merely qualitative assumptions regarding the factors affecting the intensity of X-ray reflection. It would accordingly be desirable to conduct all structure determinations by this method; but unfortunately the labor involved in its application to complex crystals, involving more than a very few parameters, makes this impossible. Furthermore, if several different atoms are present in the structure, it is often necessary to make quantitative assumptions regarding their relative reflecting powers, so that for this reason too the rigorous method cannot be used.

But complex crystals are of great interest, and it is desirable that structure determinations be carried out for them even at the sacrifice of rigor. The method which has been applied in these cases is this: one atomic arrangement among all of the possible ones is chosen, and its agreement with the experimental data is then examined. If the agreement is complete or extensive, it is assumed that the structure is the correct one. Striking regularities in the intensities of reflection from simple planes may suggest an approximate structure. This occurred in

Dickinson's study of tin tetraiodide[1]); he then considered values of the five parameters involved which differed only slightly from those suggested by the intensities of simple reflections, and found a set giving complete agreement with the Laue photographic data. On account of the large amount of experimental information accounted for by it, this structure can be confidently accepted as correct. In other cases it is necessary to make use quantitatively of relative reflecting powers or *F*-curves, and often agreement is found between the assumed structure and data from rotation photographs or ionization chamber measurements only; then the structure can usually be accepted as approximately correct, the uncertainty depending upon the paucity of the experimental data or the lack of agreement with them.

As a result of the recent increase in knowledge of the effective radii of various ions in crystals, Professor W. L. Bragg has suggested and applied[2]) a simple and useful theory leading to the selection of possible structures. His fundamental hypothesis is this: if a crystal is composed of large ions and small ions, its structure will approximate a close-packed arrangement of the large ions alone, with the small ions tucked away in the interstices. In case all of the close-packed positions are not occupied by large ions an open structure results. To apply this theory one determines the unit of structure in the usual way, and finds by trial some close-packed arrangement of the large ions of known radius (usually oxygen ions with a crystal radius of about 1,35 Å) compatible with this unit. The other ions are then introduced into the possible positions in such a way as to give agreement with the observed intensities, and if necessary the large ions are shifted somewhat from the close-packed positions. With the aid of this close-packing method Bragg and his co-workers have made a promising attack on the important problem of the structure of the silicate minerals.

During the investigation of the structure of brookite, the orthorhombic form of titanium dioxide, another method of predicting a possible structure for ionic compounds was developed. This method, which is described in detail in Section III of this paper, depends on the assumption of a coordination structure. It leads to a number of possible simple structures, for each of which the size of the unit of structure, the space-group symmetry, and the positions of all ions are fixed. In some cases, but not all, these structures correspond to close-packing of the large ions; when they do, the method further indicates

1) R. G. Dickinson, J. Am. Chem. Soc. **45**, 958. 1923.

2) W. L. Bragg and G. B. Brown, Pr. Roy. Soc., A, **110**, 34. 1926; W. L. Bragg and J. West, ibid., A, **114**, 450. 1927.

the amount and nature of the distortion from the close-packed arrangement.

The general method of investigation which we used is the following. Spectral photographs from the three pinacoids provided accurate dimensions of the possible units of structure. Data from Laue photographs then led to the determination of the smallest allowable unit, and the presence and absence of reflections on Laue photographs served as criteria in finding the space-group symmetry. (Laue photographs rather than rotation photographs were used because the chance of error in assigning indices to Laue spots is very small[1].) On applying the coordination theory we found that one of the predicted structures had the same space-group symmetry and unit of structure as the crystal itself. The predicted parameter values agreed reasonably well with the intensities of reflections on rotation photographs, and better agreement was obtained by changing one of the nine parameters slightly. On account of lack of knowledge of F-curves the intensities of Laue spots were not accounted for.

II. The unit of structure and space-group.

Three forms of titanium dioxide, TiO_2, are known. Of these the crystal structures of the two tetragonal forms, rutile and anatase, have been thoroughly investigated[2]; in each case only one parameter is involved, and the atomic arrangement has been accurately determined. The third form, brookite, is orthorhombic, with axial ratios

$$0{,}8416 : 1 : 0{,}9444.$$

Data obtained from photographs of the K-radiation of molybdenum reflected from the ground pinacoids of a brookite crystal (variety arkansite from Magnet Cove, Ark.)[3] are given in Table 1. These lead to a unit with $d_{100}/n_1 = 2{,}291$ Å, $d_{010}/n_2 = 2{,}718$ Å, and $d_{001}/n_3 = 1{,}284$ Å, in which n_1, n_2, and n_3 are the orders of reflection of the first lines on the photographs. Laue photographs were taken with the incident beam of X-rays at various small angles with the normal to (100) of a thin plate of brookite tabular on {100} (from Riedertobel, Uri Canton,

1) As an example of an incorrect space-group determination resulting from error in assigning indices to reflections on rotation photographs mention may be made of the assignment of olivine to V_h^3 by Rinne, Leonhardt, and Hentschel (Z. Krist. **59**, 548. 1924). Bragg and Brown (Z. Krist. **63**, 538. 1926) determined the space-group of olivine to be V_h^{16} and pointed out the source of the previous error.

2) L. Vegard, Phil. Mag. **1**, 1151. 1926; G. Greenwood, ibid. **48**, 654. 1924; M. L. Huggins, Phys. Rev. **27**, 638. 1926.

3) We are indebted to Mr. René Engel for the crystals used in this research.

Table I.

Spectral data.

(hkl)	Order of Reflection	Line (MoK)	Angle of Reflection	d/n
(100)	$2n_1$	β	7°54,5′	4,586 Å
	$2n_1$	α	8 53,5	4,592
	$3n_1$	α_1	13 24	4,580
	$3n_1$	α_2	13 29	4,581
	$4n_1$	γ	15 41	4,585
	$4n_1$	β	15 59	4,583
	$4n_1$	α_1	17 59	4,584
	$4n_1$	α_2	18 6	4,582
(010)	n_2	β	6 40	2,718
	n_2	α	7 30,5	2,716
	$2n_2$	γ	13 11	2,718
	$2n_2$	β	13 25	2,720
	$2n_2$	α_1	15 5	2,721
	$2n_2$	α_2	15 11	2,718
(001)	n_3	γ	13 58	1,2835
	n_3	β	14 14	1,2833
	n_3	α_1	16 0	1,2841
	n_3	α_2	16 6	1,2840

Switzerland). The short wave-length limit of X-radiation present in the incident beam was 0,24 Å; values of $n\lambda$ calculated for Laue spots on the basis of the unit obtained by putting $n_1 = n_2 = n_3 = 1$ were found often to be much smaller than 0,24 Å, so that this unit cannot be the correct one. The smallest unit which will account for the Laue data is that with $n_1 = 4$, $n_2 = 2$, $n_3 = 4$; i. e., with [1])

$$d_{100} = 9{,}166 \text{ Å}, \quad d_{010} = 5{,}436 \text{ Å}, \quad d_{001} = 5{,}135 \text{ Å}.$$

The presence of all observed Laue spots, produced by planes belonging to over two hundred different forms, is accounted for by this unit. (Representative Laue data are recorded in Table II.) No evidence was found for the existence of a larger unit; hence this unit may be accepted as the true one. All indices used in this paper (including Table II) are referred to the axes of this unit of structure. The unit contains $8\,TiO_2$; the density calculated from the X-ray data is 4,12, within the range 4,03—4,22 of the experimental determinations reported in Groth,

1) During the preparation of this manuscript, a note has appeared (A. Schröder, Z. Krist. **66**, 493. 1928) giving the dimensions of the unit of structure for brookite as $a = 9{,}136 \pm 0{,}02$, $b = 5{,}439 \pm 0{,}01$, $c = 5{,}153 \pm 0{,}03$ Å. No space-group determination or discussion of the atomic arrangement was reported.

Table II.

Laue data for $n\lambda$ between 0,35 and 0,45 Å.

(hkl)	d_{hkl}	$n\lambda$	Estimated intensity
2 $\bar{4}$ 1	1,25 Å	0,42 Å	0,02
2 1 $\bar{4}$	1,20	,36	,5
1 4 $\bar{2}$	1,18	,44	,8
1 $\bar{2}$ 4	1,15	,44	,1
3 $\bar{4}$ $\bar{2}$	1,11	,37	,5
2 $\bar{4}$ 3	1,03	,40	a
2 3 $\bar{4}$	1,02	,37	1
3 $\bar{5}$ 1	1,00	,41	0,3
1 $\bar{1}$ 5	1,00	,44	,01
1 5 $\bar{2}$	0,99	,36	,1
4 $\bar{4}$ $\bar{3}$	,96	,42	,2
3 1 $\bar{5}$	,95	,36	,2
1 $\bar{2}$ 5	,95	,35	,1
2 5 $\bar{3}$	,89	,42	,4
4 $\bar{2}$ $\bar{5}$	,88	,35	,8
3 $\bar{5}$ 3	,87	,40	,5
2 $\bar{3}$ 5	,87	,41	,05
3 3 $\bar{5}$	,85	,38	,05
1 $\bar{1}$ 6	,84	,35	,15
1 1 6	,84	,43	,2
4 $\bar{6}$ 1	,83	,39	,15
5 $\bar{5}$ $\bar{3}$	,82	,41	,2
5 $\bar{6}$ $\bar{1}$	,80	,43	,1
3 $\bar{5}$ 4	,80	,37	,02
3 5 $\bar{4}$	,80	,43	,03
1 6 3	,79	,45	,2
5 $\bar{6}$ $\bar{2}$	,77	,36	,15
1 3 6	,77	,42	,2
2 7 $\bar{1}$	,75	,43	,05
1 5 5	,74	,42	,02
1 7 2	,74	,39	,2
1 4 6	,72	,40	,2
5 3 $\bar{6}$	,71	,45	,05
1 2 7	,70	,36	,1
2 $\bar{2}$ 7	,70	,35	,01
2 2 7	,70	,45	,05
3 $\bar{2}$ 7	,69	,44	,15
3 7 $\bar{3}$	,68	,40	,05
5 $\bar{7}$ 2	,68	,37	,05
7 $\bar{3}$ $\bar{6}$	,66	,43	,1
7 $\bar{7}$ $\bar{1}$	,66	,45	a
2 7 4	,65	,44	0,2
3 8 $\bar{1}$	,65	,44	,05

Table II (cont.).

(hkl)	d_{hkl}	$n\lambda$	Estimated intensity
4 6 $\bar{5}$	0,65 Å	0,38 Å	0,1
7 $\bar{7}$ $\bar{2}$	,64	,41	,15
7 $\bar{1}$ $\bar{7}$	,63	,41	,1
7 $\bar{2}$ $\bar{7}$	,62	,37	,03
6 $\bar{7}$ 4	,61	,41	,1
5 $\bar{4}$ 7	,61	,45	,05
4 8 $\bar{3}$	,60	,41	,03
2 9 8	,60	,37	,1
5 6 $\bar{6}$	,59	,36	,02
7 $\bar{8}$ 3	,57	,39	,04
3 7 6	,56	,43	,05
7 5 $\bar{7}$	,55	,41	,05
9 $\bar{4}$ $\bar{7}$	,54	,38	,02
4 2 9	,54	,43	,03
4 4 9	,51	,41	,03
5·10·2	,51	,45	,02
5·10·$\bar{2}$	,51	,39	,02
10·$\bar{1}$·$\bar{9}$	,47	,36	,02
10·1·9	,47	,38	,03

and in good agreement with the experimental value 4,125 obtained by Schröder.

The presence of first-order reflections from all types of pyramidal planes (Table II) eliminates from consideration all space-groups based on any but the simple orthorhombic lattice Γ_0. Of these the following are further definitely eliminated[1]) by the occurrence of first-order reflections from the prism planes given in Table III:

$$C_{2v}^3,\ C_{2v}^6,\ C_{2v}^7,\ C_{2v}^8,\ C_{2v}^9,\ C_{2v}^{10},$$
$$V_h^2,\ V_h^4,\ V_h^6,\ V_h^7,\ V_h^8,\ V_h^9,\ V_h^{10},\ V_h^{12},\ V_h^{13},\ V_h^{14},\ V_h^{16}.$$

If the structure is based on one of the space-groups

$$C_{2v}^1,\ C_{2v}^2,\ C_{2v}^4,\ C_{2v}^5,\ V^1,\ V^2,\ V^3,\ V^4,\ V_h^1,\ V_h^3,\ V_h^5,\ \text{or}\ V_h^{11},$$

it is very difficult to account for the fact that no first-order reflections were observed from planes with $h = 0$ and k odd, $k = 0$ and l odd, or $l = 0$ and h odd; these space-groups may accordingly be removed from consideration. But just these absences are required for any arrangement derived from V_h^{15}, which may hence be accepted as the correct space-group.

1) Space-group criteria are given by Bozorth and Pauling, J. Am. Chem. Soc. **47**, 1568. 1925. Cf. also references in ootnote 13, ibid.

Table III.

Prism reflections.

a) Incident beam normal to (100).

(hkl)	d_{hkl}	$n\lambda$	Estimated intensity
1 4 0	1,33 Å	0,43 Å	a
1 0 4	1,26	,33	0,15
1 0 $\bar{4}$	1,26	,37	,20
2 0 5	1,00	,43	a
2 0 $\bar{5}$	1,00	,45	a
2 7 0	0,76	,28	0,03
4 7 0	,73	,49	a
4 $\bar{7}$ 0	,73	,44	a
4 0 $\bar{7}$	,70	,42	a
5 0 $\bar{8}$	,60	,41	0,02
b) Crystal tipped 14°.			
0 3 1	1,70	0,47	a
0 3 2	1,47	,44	a
0 2 3	1,44	,42	3,5
0 4 1	1,31	,35	1,2
1 5 0	1,07	,48	a
0 4 3	1,06	,32	1,8
0 3 4	1,04	,31	a
1 0 5	1,01	,43	a
1 0 6	,85	,33	0,3
0 5 4	,82	,24	a
0 4 5	,81	,24	a
2 7 0	,76	,41	0,6
6 $\bar{7}$ 0	,69	,48	,2
3 0 8	,63	,38	,1
c) Crystal tipped 20°.			
0 2 $\bar{1}$	2,39	0,29	2
0 4 1	1,31	,47	1,9
0 4 $\bar{1}$	1,31	,27	0,5
0 1 4	1,24	,44	a
0 4 3	1,06	,44	0,3
0 5 1	1,06	,36	a
0 5 $\bar{1}$	1,06	,24	a
0 3 4	1,04	,43	a
3 $\bar{5}$ 0	1,02	,39	a
0 1 5	1,00	,34	a
3 0 $\bar{5}$	,97	,34	a
0 2 5	,96	,36	0,2
4 0 $\bar{5}$	,93	,49	a
1 0 6	,85	,40	0,5
0 5 4	,82	,34	a
0 4 5	,82	,33	0,1

Table III (cont.).

c) Crystal tipped 20° (cont.).

(hkl)	d_{hkl}	$n\lambda$	Estimated intensity
5 $\bar{6}$ 0	0,81 Å	0,47 A	a
5 0 $\bar{6}$	,77	,42	0,2
2 7 0	,76	,47	,6
1 0 7	,73	,32	a
2 0 7	,72	,43	a
6 $\bar{7}$ 0	,69	,42	0,17
3 0 8	,63	,43	,1
7 $\bar{8}$ 0	,60	,39	a
2 9 0	,59	,32	0,02
3 8 0	,50	,35	a

The coordinate positions for equivalent atoms provided by V_h^{15} are[1])

4a: 0 0 0; $\frac{1}{2}\ \frac{1}{2}\ 0$; $0\ \frac{1}{2}\ \frac{1}{2}$; $\frac{1}{2}\ 0\ \frac{1}{2}$;
4b: $\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$; $0\ 0\ \frac{1}{2}$; $\frac{1}{2}\ 0\ 0$; $0\ \frac{1}{2}\ 0$;
8c: x, y, z; $\bar{x}, \bar{y}, \bar{z}$; $\frac{1}{2}+x, \frac{1}{2}-y, \bar{z}$; $\frac{1}{2}-x, \frac{1}{2}+y, z$;
$\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$; $x, \frac{1}{2}-y, \frac{1}{2}+z$; $\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z$;
$\frac{1}{2}+x, y, \frac{1}{2}-z$.

Six parameters must be evaluated to determine the positions of $8\,Ti$ and $16\,O$ in the unit in case that both the no-parameter positions 4a and 4b are occupied, and nine parameters in case that all atoms are in positions 8c. A structure dependent on such a large number of parameters can not be determined by rigorous methods.

III. The prediction of a structure with the coordination theory.

The structures of rutile and anatase, represented in Figs. 1 and 2, seem at first sight to have very little in common beyond the fact that each is a coordination structure, with six oxygen atoms about each titanium atom and three titanium atoms about each oxygen. On closer examination, however, it is found that from a certain point of view the structures are closely similar. Let us consider as the basis of the structures an octahedron with a titanium atom at its center and an oxygen atom at each corner. The rutile and anatase structures are both made of such octahedra sharing edges and corners with each other; in rutile two edges of each octahedron are shared and in anatase four. In both crystals the titanium-oxygen distance is a constant, with

1) R. W. G. Wyckoff, "The Analytical Presentation of the Results of the Theory of Space-Groups", Publ. Carnegie Institution No. 318, 1922.

the value 1,95—1,96 Å. The basic octahedra are only approximately regular; they are in both rutile and anatase deformed in such a way as to cause each shared edge to be shortened from 2,76 Å (the value for regular octahedra) to 2,50 Å, other edges being correspondingly lengthened. (The distorted octahedra occurring in rutile and in anatase are indicated in Figs. 1 and 2.) Just such a distortion is to be expected, for the Coulomb repulsion of the two quadrivalent metal ions brought near each other when an edge is shared will cause the titanium-titanium distance to increase until the repulsion of the two oxygen ions defining

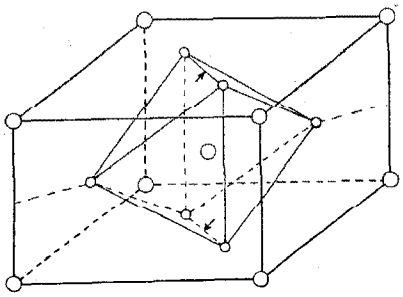

Fig. 1.

Fig. 1. The structure of rutile. Large circles represent the centers of titanium atoms, small circles those of oxygen atoms. One octahedron with oxygen atoms at its cornex and a titanium atom at its center is shown; two of its edges, those indicated by arrows, are shared with adjoining octahedra.

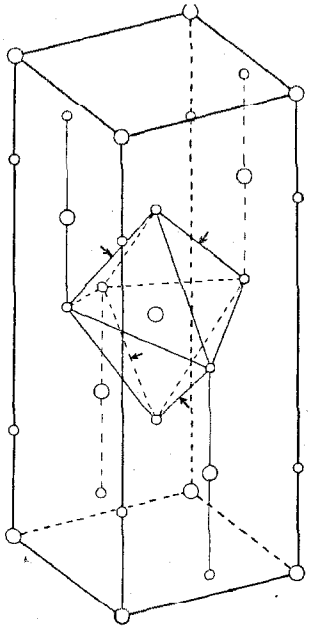

Fig. 2.

Fig. 2. The structure of anatase. Four edges of the octahedron shown, indicated by arrows, are shared with adjoining octahedra.

the shared edge becomes large enough to counteract the effect. The theoretical discussion[1]) of the rutile and anatase structures with the help of the known properties of ions has led to results which are in each case in quantitative agreement with the observed contraction of shared edges.

As a result of these considerations the following assumptions were made:

1. Brookite is composed of octahedra, each with a titanium atom at its center and oxygen atoms at its corners.

1) Linus Pauling, Z. Krist. **68**, 377. 1928.

2. The octahedra share edges and corners with each other to such an extent as to give the crystal the correct chemical composition.

3. The titanium-oxygen distance throughout is about 1,95 Å. The octahedra are not regular, but are distorted in such a way as to maintain the titanium-oxygen distances constant and to shorten each shared edge to the length 2,50 Å.

An infinite number of structures satisfy these conditions. The number of simple structures, that is, structures referable to a small unit, which do so is small. We made no attempt to consider exhaustively the possible simple structures, but instead investigated the two which presented themselves first. The second of these we have found to be the structure of brookite.

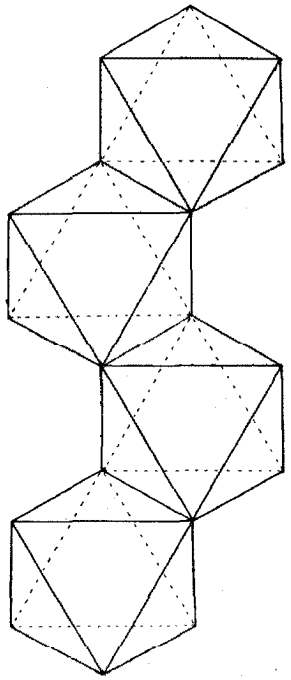

Fig. 3. A staggered string of octahedra with shared edges.

In rutile there occur strings of octahedra in parallel orientation connected by shared edges; these strings, which extend in the direction of the c-axis, then are connected by sharing corners to form the complete crystal. This suggested that staggered strings such as are represented in Fig. 3, with two edges of each octahedron shared, might combine to form a reasonable structure. If the combination is effected by the sharing of corners alone the simple structure represented in Fig. 4 results. This structure, Structure A, has orthorhombic symmetry, and in fact the space-group symmetry V_h^{14}. Its unit of structure contains four octahedra ($4\,TiO_2$), and, if distortion is neglected, has the dimensions 4,79 Å, 4,54 Å, and 5,52 Å. It is not the structure of brookite.

The next simplest structure built from these staggered strings results if each octahedron shares one edge with an octahedron of an adjoining string. This structure is shown in Fig. 5. It is orthorhombic, and has the space-group symmetry V_h^{15}. The unit of structure contains eight octahedra ($8\,TiO_2$). Its dimensions, if the octahedra are assumed regular with edges 2,76 Å long, are $d_{100} = 9{,}02$ Å, $d_{010} = 5{,}52$ Å, and $d_{001} = 4{,}79$ Å. The space-group permits cyclical but not non-cyclical permutations of these dimensions.

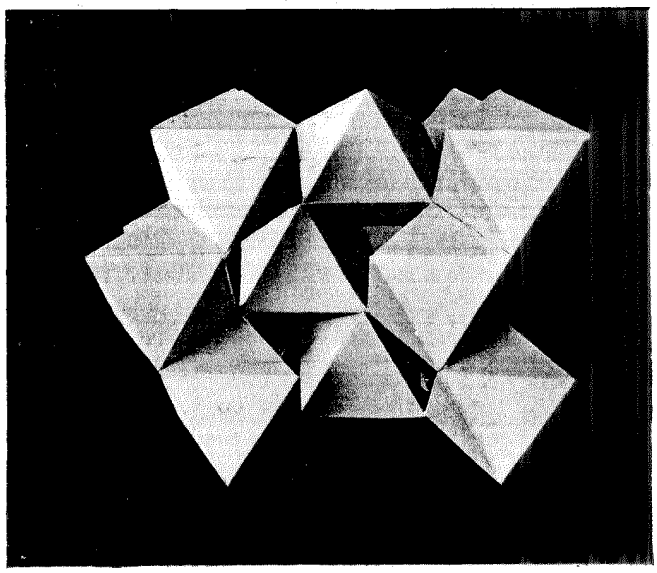

Fig. 4. A model representing a possible structure for TiO_2 (Structure *A*), composed of staggered strings of octahedra (Fig. 3) combined by sharing octahedron corners only.

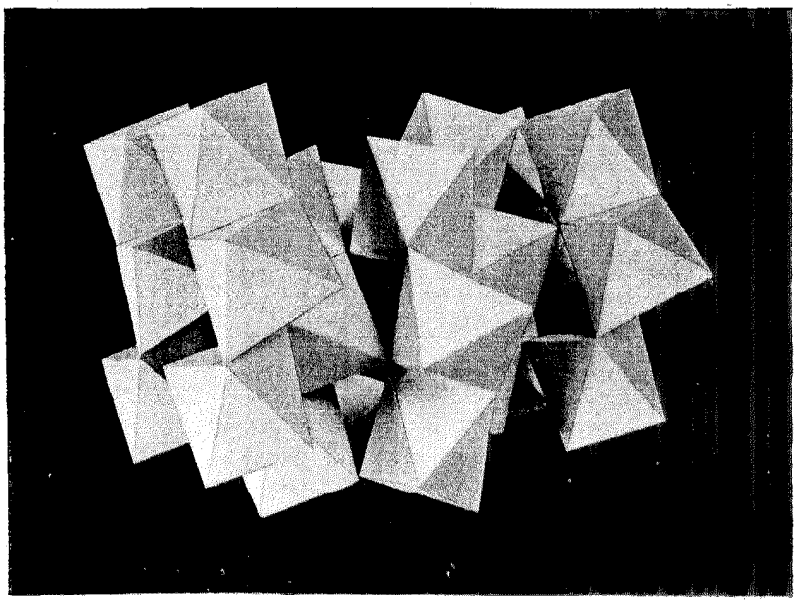

Fig. 5. A photograph of the model representing the structure of brookite.

The fact that brookite also was found experimentally to have the symmetry of V_h^{15} and to have $8\,TiO_2$ in the unit suggests strongly that our second structure is to be attributed to this crystal. There is also approximate agreement (within 7%) in the dimensions of the unit. It is worthy of mention that the choice of axes for comparison is not completely arbitrary: assuming that 9,02 Å (model) is to be compared with 9,166 Å (crystal), then the space-group requires that 5,52 Å be compared with 5,436 Å and 4,79 Å with 5,135 Å.

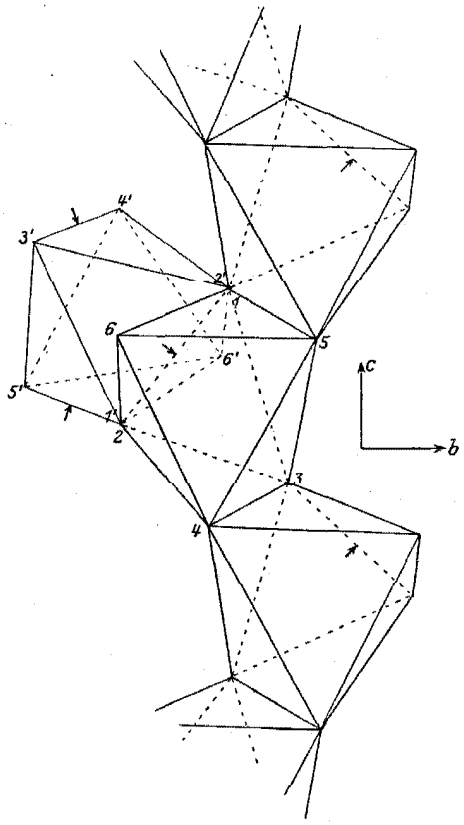

Fig. 6. A portion of the brookite structure, showing the three edges of each octahedron which are shared with adjoining octahedra, and the resulting deformation.

Since the analytical consideration of the effect of deformation appearedto be too complicated to permit its execution, the following method based upon the construction and measurement of a model was used. The basic distorted octahedron employed is shown in Fig. 6; in it all titanium-oxygen distances are equal to 1,95 Å; the three shared edges are 2,50 Å long; and the other edges are chosen so as to be distorted as little as possible from their original lengths. Such octahedra were constructed to scale (2,54 cm. = 1 Å) from heavy paper, and were then glued together to represent a section of the crystal including one unit of structure (Fig. 5). The carefully measured dimensions of the unit were found to be 23,65 cm., 14,0 cm., and 13,2 cm.; if these are reduced in the ratio 2,57 cm. = 1 Å (the increase in scale being due to incomplete coincidence of edges and corners of the octahedra) they give the values shown in Table IV, which agree within the limit of error of the measurement with the experimental values for brookite.

The suggested structure places eight titanium atoms and two groups of eight oxygen atoms each in the positions 8c, with three sets of

Table IV.

Dimensions of the unit of structure.

	d_{100}	d_{010}	d_{001}
From model, with undistorted octahedra	9,02 Å	5,52 A	4,79 A
From model, with distorted octahedra	9,20	5,45	5,13
Experimental, for brookite	9,166	5,436	5,135

parameter values. In order to predict values of these parameters the coordinates of the oxygen atoms were measured on the model, and positions were assigned the titanium atoms in the octahedra such as to make the titanium-oxygen distances nearly constant. Representing by x, y, z; ξ, η, ζ; and X, Y, Z the parameters for oxygen of the first kind, oxygen of the second kind, and titanium, respectively, the values that were predicted are

O_1	O_2	Ti
$x = 0{,}010$	$\xi = 0{,}230$	$X = 0{,}131$
$y = 0{,}155$	$\eta = 0{,}105$	$Y = 0{,}113$
$z = 0{,}180$	$\zeta = -0{,}465$	$Z = -0{,}127.$

These may be compared with those corresponding to undistorted octahedra, namely,

O_1	O_2	Ti
$x = 0{,}000$	$\xi = 0{,}250$	$Y = 0{,}125$
$y = 0{,}124$	$\eta = 0{,}125$	$Y = 0{,}125$
$z = 0{,}250$	$\zeta = -0{,}417$	$Z = -0{,}083.$

It is seen that the parameter changes due to distortion are considerable, being equivalent to translations of atoms as large as 0,35 Å.

IV. Testing the structure with the intensities of X-ray reflections.

A number of rotation photographs were made with molybdenum K-radiation filtered through a zirconium oxide filter to isolate the $K\alpha$ line. The positions of useful reflections, the indices of the planes producing them, and their visually estimated intensities are given in Table V. The factor placed beside the estimated intensity is a correction for the varying time of reflection, namely $\sqrt{1 - (u\lambda/d \sin 2\theta)^2}$, where λ is the wave-length, and u and d represent respectively the index of the axis of rotation and the unit translation along it[1]. (A number of reflections

1) Ott, Z. Phys. **22**, 201. 1924.

not included in the tables occurred on each photograph; namely, those produced by planes whose traces in the developed or ground face of the crystal [the faces (100), (010), and (001) for Table V] were not perpendicular to the axis of rotation of the crystal. These reflections were not considered because of the probability that their intensities would be largely affected by absorption in the crystal.)

Table V.

Spectral reflections[1].

a) Planes of form $(0kl)$.

1. Beam incident on (0 1 0).

$k=$	2	4	6
$l=0$	w 1	s 17	w 4

2. Beam incident on (0 0 1).

$l=$	2	4	6
$k=0$	a 0,8	mw 9	vw 5

b) Planes of form $(h0l)$.

1. Beam incident on (1 0 0)

$h=$	2	4	5	6	7	8	9	10	12	14
$l=0$	vvw 0,2	ms 3,5		w 1,7		vs 17		a 0,5	mw 8	w 5,5
$l=2$			s 0,8 12	w 0,8 3,5	mw 0,9 4	vvw 0,9 3	mw 0,9 12	a 3,5		

2. Beam incident on (0 0 1)

$l=$	2	4	6
$h=1$	m 6,5	vw 3,5	w 12
$h=2$	mw 0,9 6	a 0,6	a 2,5
$h=3$	mw 0,8 7	a 3	
$h=4$		mw 0,9 12	

1) The estimated intensities of the various reflections are indicated by the abbreviations vs, very strong; s, strong; ms, medium strong; m, medium; mw, medium weak; w, weak; vw, very weak; vvw, very very weak; a, absent. The number placed below the estimated intensity for each plane gives the computed structure-factor.

c) Planes of form $(hk0)$.

1. Beam incident on (1 0 0)

$h =$	2	4	6	8	10
$k = 1$	s 0,7 8	vw 0,9 2	m 4	a 3	m 10
$k = 2$		w 0,8 2	a 1,5	vw 0,9 0,7	a 2,5

2. Beam incident on (0 1 0)

$k =$	1	2	3	4	5	6	7
$h = 2$	s 0,7 8	vw 0,9 2,5	s 0,9 10	a 0,8	a 5	a 6,5	a 11
$h = 4$		w 0,6 2,5	a 0,2	vw 0,9 4	a 0,4	mw 0,9 6	

Structure factors were calculated with the use of the predicted parameter values and with the assumption that the relative reflecting powers of titanium and oxygen atoms are proportional to their atomic numbers. These structure factors reproduced the salient features of the observed intensities for fifty forms; this general agreement is strong evidence that the predicted structure closely approximates the actual one. There was, however, disagreement in a few cases, when one reflection was observed to be stronger than another from a plane with larger interplanar distance despite the fact that its calculated structure factor was the smaller of the two. Accordingly, the parameter values were varied slightly, and a change of $-0{,}004$ in X was found sufficient to remove most of the points of discrepancy. Structure factors calculated for the new parameter values with the assumption of relative reflecting powers proportional to atomic numbers are included in Table V. It will be seen that when qualitative consideration is taken of the effect of other factors causing a decrease in intensity with decrease in interplanar distance, the agreement for all fifty forms is good. The changed parameter values given in Table VI may accordingly be accepted as correct.

Table VI.

Final parameter values for brookite.

O_1	O_2	Ti
$x = 0{,}010$	$\xi = 0{,}230$	$X = 0{,}127$
$y = 0{,}155$	$\eta = 0{,}105$	$Y = 0{,}113$
$z = 0{,}180$	$\zeta = -0{,}465$	$Z = -0{,}127$

The few remaining discrepancies are probably due to error in the assumed relative reflecting powers. To test this, we made use of an F^2-curve for $O^=$ obtained by linear extrapolation from Na^+ and Cl^-, and one for Ti^{4+} from Cl^- and K^+. These F^2-curves (which are not reproduced here because of uncertainty in their derivation) lead to structure factors which are, for the same final parameter values, also in good but not complete agreement with the observed intensities. Possibly somewhat different F^2-curves (corresponding to non-linear extrapolation) would give better agreement, but because of the arbitrariness of this procedure no attempt was made to utilize it.

It is worthy of mention that the rotation photographs yield information substantiating the choice of T_h^{15} as the correct space-group. Thus no reflections occurred from {100}, {300}, {500}, {700}, {900}, {11·0·0}, {13·0·0}, {301}, {501}, {701}, {901}, {11·0·1}, {401}, {601}, {801}, {10·0·1}, {12·0·1}, etc. on one photograph recorded in Table V, although planes of all these forms were in positions favorable to reflection. Similar failures to reflect were observed on the other photographs.

On account of the lack of definite knowledge of the F^2-curves no attempt was made to account for the intensities of Laue spots.

V. Discussion of the structure and the coordination method.

The structure found for brookite is that shown in Fig. 5. Each titanium atom is surrounded by six oxygen atoms and each oxygen by three titanium atoms. The various interatomic distances, given in Table VII, are similar to those in rutile and anatase; for example, the average titanium-oxygen distance is 1,95 Å. The oxygen-oxygen distances and the distortion of the basic octahedra have been discussed in the previous sections in the course of derivation of the structure.

Table VII.

Interatomic distances in brookite.

$Ti-O_1$	1,949 Å	O_1-O_3	2,767 Å
$Ti-O_2$	1,942	O_2-O_3	2,818
$Ti-O_3$	1,929	O_2-O_4	2,997
$Ti-O_4$	1,976	O_2-O_6	2,817
$Ti-O_5$	1,983	O_3-O_5	2,731
$Ti-O_6$	1,953	O_3-O_4	2,514
		O_4-O_5	3,042
O_1-O_2	2,508	O_4-O_6	2,833
O_1-O_3	2,869	O_5-O_6	2,743
O_1-O_5	2,514		

We believe that our conclusions can be accepted with considerable certainty, for the agreement between the predicted structure and the experimental results in regard to space-group symmetry, size of the unit of structure, and intensities of reflections on rotation photographs is so striking as to remove nearly completely from consideration the possibility of its being accidental.

The arrangement of the oxygen atoms approximates double hexagonal close-packing[1]). It is evident, then, that Bragg's close-packing method of deriving a possible structure might have been used. But both hexagonal and double hexagonal close-packing of oxygen ions are roughly compatible with the observed unit (compare Rows 1 and 3 of Table IV). To decide between these possibilities intensity comparisons would be required, and in the absence of information regarding the nature of the deformation from regular close-packing this procedure might be very laborious. In anatase the oxygen ions approximate cubic close-packing; the axial ratio is, however, increased from 2,0 to 2,5 by deformation, and a knowledge of the size of the unit of structure would not suggest the close-packed arrangement with much certainty. Rutile provides an example of a structure which is easily derivable by means of the coordination theory, but in which the oxygen ions do not approach any type of close-packing whatever.

The close-packing method is more generally applicable in the case of crystals containing cations smaller than the titanium ion and showing correspondingly less deformation. The method is very powerful and simple, and already in the hands of Professor Bragg has led to a number of interesting structure determinations. The coordination method, though also simple in principle, is somewhat less easy to apply. The two methods are not distinct and mutually exclusive, but instead supplement each other and should be used together.

VI. Summary.

Brookite, TiO_2, is found with the use of Laue and spectral photographs to have an orthorhombic unit of structure with $d_{100} = 9{,}166$ Å, $d_{010} = 5{,}436$ Å, and $d_{001} = 5{,}135$ Å, containing $8\,TiO_2$, and to have the symmetry of space-group V_h^{15}. A structure predicted by means of the

1) There are three close-packed layers from which all of the infinite number of close-packed structures can be built; namely, A, with an atom at $X = 0$, $Y = 0$ (X, Y, Z being hexagonal coordinates); B, with an atom at $X = \frac{1}{3}$, $Y = \frac{2}{3}$; and C, with an atom at $X = \frac{2}{3}$, $Y = \frac{1}{3}$. For hexagonal close-packing these layers are superposed in the order $ABABAB\ldots$, for cubic close-packing in the order $ABCABC\ldots$, and for double hexagonal close-packing in the order $ABACABAC\ldots$

coordination theory had the same unit and space-group symmetry, and gave an atomic arrangement accounting for the intensities observed on rotation photographs. In this structure the eight titanium atoms and the sixteen oxygen atoms (in two groups of eight each) are in positions 8*e* with the parameter values given in Table VI. The basic unit of the arrangement is an octahedron of oxygen ions about a titanium ion; the octahedra are combined as shown in Fig. 5 so that each shares three edges with adjoining ones. Interatomic distances are given in Table VII.

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J. H. Sturdivant and **Linus Pauling** (Pasadena): **Note on the Paper of A. Schröder: Beiträge zur Kenntnis des Feinbaues des Brookits usw.** (With 2 figures.)

We have recently found[4]) the space-group symmetry of brookite, the orthorhombic form of titanium dioxide, to be that of V_h^{15}. In our space-group determination, use was made of the presence or absence of reflections on Laue photographs only. Reflections from all types of bipyramidal planes were observed, requiring that the structure be based on the simple orthorhombic lattice Γ_0. No first-order reflections were observed from prism planes of the following classes, although many such planes were in positions favorable to reflection:

$$k = 0 \text{ and } l \text{ odd};$$
$$l = 0 \text{ and } h \text{ odd};$$
$$h = 0 \text{ and } k \text{ odd}.$$

The space-group criteria for V_h^{15} are that no odd-order reflections shall occur from just these planes. These criteria were afterwards found to be satisfied by reflections observed on several rotation photographs.

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1) Gemeint ist dabei die Deformation der farblosen gelösten Ionen Hg^{++} und J^- bei ihrer Vereinigung zum Salz.
2) H. Ley, Z. angew. Ch. **41**, 845. 1928.
3) G. Scheibe, Chem. Zentralbl. 1927, II. 2151. Z. Elektrochem. **34**, 497. 1928.
4) Linus Pauling and J. H. Sturdivant, Z. Krist. **68**, 239. 1928.

On page 241 of our paper we pointed out the desirability of basing a space-group determination on Laue photographs rather than on rotation photographs, on account of the small chance of error in assigning indices to the planes producing Laue spots and the much larger uncertainty in identifying planes producing reflections on rotation photographs. An example of an incorrect choice of space-group arising from the use of rotation photographs was cited.

A. Schröder[1]) has published data on rotation photographs of brookite which are incompatible with the space-group V_h^{15}. He reports the observation of odd-order reflections from the following classes of prism planes:

$$k = 0 \text{ and } l \text{ even},$$
$$l = 0 \text{ and } h \text{ even},$$
$$h = 0 \text{ without restriction.}$$

Reflections reported by Schröder which do not satisfy the criteria for V_h^{15} are: (051), (032), (052), (013), (033), (012), (015), (031), (034).

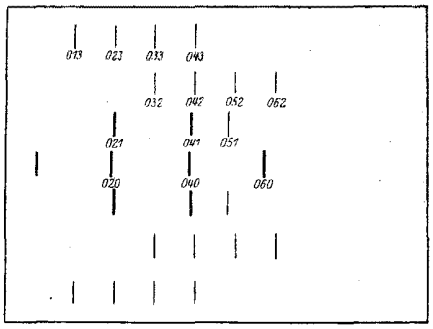

Fig. 1.

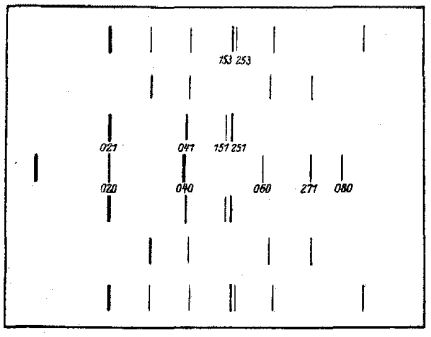

Fig. 2.

Fig. 1. Diagram of Schröder's rotation photograph No. 3, showing his assignment of indices. The X-ray beam was incident on (010), the crystal rotating through 20° about [001].

Fig. 2. Diagram of a photograph made by the writers with the crystal oriented as for Fig. 1, but rotating through 45°. The proper assignment of indices is shown for those lines which it is considered practical to identify.

On our Laue photographs the following planes, listed in Table III of our paper, failed to reflect in the first order, although in position to do so: (051), (05$\bar{1}$), (032), (015), (031), (034). The following planes not listed in our paper also failed to produce Laue spots, although in a position to reflect radiation of the wave-lengths indicated: (052) at $n\lambda = 0{,}28$ and 0,38 Å, (013) at $n\lambda = 0{,}59$ Å, (012) at $n\lambda = 0{,}64$ Å. These observations show that eight of the nine reflections reported by Schröder to disagree with the criteria of V_h^{15} do not occur on Laue photographs. The presence or absence of the remaining reflection, (033), cannot be determined from Laue photographs on account of its superposition on (022).

There is additional evidence that Schröder's supposed observation of reflections which we find not to occur arose from error in his assignment

1) A. Schröder, Z. Krist. **67**, 485. 1928.

of indices to reflections on rotation photographs. The distance between reflections due to planes of form $(0kl)$ and of form $(1kl)$ on a photograph made with the film 10 cm. from the crystal is 0,7 mm. Measurements of the position of the central point of a given line referred to the central point of the undeviated image can accordingly scarcely be rendered sufficiently trustworthy to decide between two possible sets of indices differing so slightly as $(1kl)$ and $(0kl)$. The distance between two reflections which lie close together, however, can afford a more decisive test. We have made a rotation photograph with the X-ray beam incident on the (010) plane of brookite, and with the crystal rotating through 45° about the c-axis; the crystal-to-film distance was 10 cm. and the $MoK\alpha$ radiation was isolated with a zirconia filter. This photograph corresponds to Schröder's photograph No. 3, reproduced with his assignment of indices in fig. 1. On our photograph, the principal reflections of which are represented in fig. 2, there appears on the right of the line numbered (051) by Schröder a slightly stronger reflection. These two reflections are due to two of the planes (051), (151), and (251). In both lines, the $K\alpha$ doublet was resolved. We calculate the following theoretical separations for the $MoK\alpha_1$ reflections from these planes:

(051) to (151) = 0,074 cm.
(051) to (251) = 0,221 cm.
(151) to (251) = 0,147 cm.

The separation of the two $K\alpha_1$ reflections was measured on the film as 0,143 ± 0,003 cm. These two reflections are accordingly due to the planes (151) and (251), and Schröder's assignment of one of them to the prism plane (051) is incorrect[1]).

The same error was no doubt made in his assignment of indices to the other reflections.

Summary.

It is shown that Schröder's reported observation of X-ray reflections from brookite not allowed for a structure based on the space-group V_h^{15} is due to error in his assignment of indices to lines on rotation photographs.

Gates Chemical Laboratory, California Institute of Technology.
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1) The occurrence on Schröder's photograph of the reflection from (151) and not that from (251) arises from his small angle of oscillation of the crystal (20°).

THE CRYSTAL STRUCTURE OF COLUMBITE

Columbite and tantalite[1] form a series of mixed crystals of composition $(Fe,Mn)(Cb,Ta)_2O_6$, with orthorhombic holohedral symmetry. The crystal used in the present investigation was a short columbite prism from Norway,[2] showing developed pinacoids, black, with a density of 5.71 ± 0.1 (determined on a powdered sample with a pycnometer). Laue and oscillation photographs prepared with it served for determining the space group and unit cell, while to find possible atomic positions use was made of the coördination theory and of close packing.

I. The Unit Cell and Space Group

Oscillation photographs for the determination of the lattice constants were made with molybdenum K-radiation reflected from the pinacoids, a calcite spectrum being recorded simultaneously for a comparison. Table I shows the data obtained. The indices of the reflecting pinacoids are referred to axes which will later be seen to be indicated by the space group with Wyckoff's distribution of symmetry

elements; the space group axes are related to the crystallographic axes (after Dana) by cyclic permutation: $\underline{a}_{Dana} \backsim \underline{b}$, $\underline{b}_{Dana} \backsim \underline{c}$, $\underline{c}_{Dana} \backsim \underline{a}$. The tabulated interferences lead to a unit with $d_{100}/n_1 = 2.541$ Å, $d_{010}/n_2 = 7.119$ Å, $d_{001}/n_3 = 2.865$ Å; n_1, n_2, and n_3 are the orders of reflection of the first lines on the respective photographs. Laue photographs were taken with the incident beam of X-rays inclined at various small angles to the normals of three thin slips ground parallel to (100), (010), and (001), respectively. The short wavelength limit of the incident spectrum (from a tungsten target) was 0.24 Å. The smallest unit which will give calculated values of $n\lambda$ not less than 0.24 Å for all Laue spots is that corresponding to $n_1 = n_2 = n_3 = 2$; since this unit accounts for all reflections observed on the two Laue photographs which were completely analyzed, it is to be accepted as the correct one. (Table II lists a few typically useful Laue interferences appearing on one photograph; on the two photographs mentioned, a total of approximately two hundred forms reflected.) The fundamental translations are:

$$d_{100} = 5.082 \text{ Å}, \quad d_{010} = 14.238 \text{ Å}, \quad d_{001} = 5.730 \text{ Å}.$$

These are confirmed by the application of the Polanyi formula $\frac{r}{\lambda}$ to the layer lines occurring on all oscillation photographs. All indices occurring in this paper are referred to the axes

Table I

Measurements of the axial lengths

(hkl)	Order	Line (Mo K)	ϑ	d/n	Average
(100)	n_1	β	7° 8. '	2.542 Å	
	n_1	α	8 1.5	2.543	
	2 n_1	β	14 24.	2.540	
	2 n_1	α_1	16 11.	2.541	
	2 n_1	α_2	16 17.	2.541	2.541 Å
(010)	2 n_2	α	5 43.5	7.117	
	3 n_2	β	7 38.5	7.120	
	3 n_2	α_1	8 35.	7.119	7.119
(001)	n_3	β	6 19.5	2.865	
	n_3	α	7 6.5	2.868	
	2 n_3	α_1	14 19.	2.863	
	2 n_3	α_2	14 24.	2.864	2.865

Table II

Selected first-order pyramidal reflections

from a typical Laue photograph

X-ray beam at small angle to (010); 170 mah., 51.5 kv. peak.

Form {hkl}	nλ Å
311	.40, .44
434	.30, .35, .38, .43
335	.30, .33, .39, .43
136	.30, .31, .41, .42
435	.24, .28, .35, .31
337	.25, .27
731	.24, .25
762	.35, .37, .40, .41
499	.32, .34, .38, .40
895	.31, .34, .35, .38

of this unit of structure.

The axial ratio calculated from the X-ray data is a:b:c = 0.3569 : 1 : 0.4024. This may be compared with the axial ratio given by Dana for a columbite crystal:[3] $a_{Dana}:b_{Dana}:c_{Dana}$ = 0.82850 : 1 : 0.88976, or a:b:c = 3 x 0.3580 : 1 : 3 x 0.4023.

If the crystal were pure columbite, with any ratio of iron to manganese, the observed unit would contain 4.24 molecules of $(Fe,Mn)Cb_2O_6$. The composition $(Fe,Mn)Ta_2O_6$, corresponding to pure tantalite, would require 2.79 molecules in the unit cell. The unit cell must therefore contain either three or four molecules of $(Fe,Mn)M_2O_6$. With the former alternative, the specimen must consist of 73.5% Ta_2O_5, 11.5% Cb_2O_5; with the latter, of 14.1% Ta_2O_5, 65.8% Cb_2O_5. A decision between the two possibilities may be made by reference to Marignac's table showing the relation between density and composition of columbites and tantalites[4] (or to other summaries of analytical results):

Density	5.36	5.65	5.70	5.74	5.92
Percent Ta_2O_5	3.3	15.8	13.8	13.4	27.1
			6.05	...	7.03
			30.4	...	65.6

The former composition is correlated with a density of 7;

the latter with a density of 5.7. The unit of columbite therefore contains four molecules.

Since first-order Laue reflections are observed from all types of pyramidal planes (Table II), the space group is based on the simple orthorhombic lattice Γ_o. Of the space groups derived from Γ_o the following are eliminated[5] by observed first-order reflections on Laue photographs from the prism planes listed in Table III: C_{2v}^3, C_{2v}^8, C_{2v}^9, C_{2v}^{10}, V_h^2, V_h^3, V_h^4, V_h^6, V_h^8, V_h^9, V_h^{10}, V_h^{12}, V_h^{15}.

Of the remaining seventeen space groups, only one requires the first-order absences which were regularly observed; namely, forms having

$$h = 0,\ k + \ell \text{ odd},$$
$$k = 0,\ \ell \text{ odd, or}$$
$$\ell = 0,\ h \text{ odd}.$$

These absences are exactly those required for any structure based on V_h^{14}, and therefore this is taken to be the correct space group. No observable reflections upon the oscillation photographs contradict the preceding conclusion; over one hundred absences upon them confirm it.

The four groups of coördinate positions permitted by V_h^{14} for equivalent atoms are:[6]

4a: $0,0,0;\ \frac{1}{2},\frac{1}{2},\frac{1}{2};\ 0,\frac{1}{2},\frac{1}{2};\ \frac{1}{2},0,0.$

4b: $\frac{1}{2},0,\frac{1}{2};\ 0,\frac{1}{2},0;\ \frac{1}{2},\frac{1}{2},0;\ 0,0,\frac{1}{2}.$

4c: $\frac{3}{4},0,u-\frac{1}{4};\ \frac{1}{4},\frac{1}{2},\frac{3}{4}-u;\ \frac{1}{4},0,\frac{1}{4}-u;\ \frac{3}{4},\frac{1}{2},u+\frac{1}{4}.$

Table III

Prism reflections on Laue photographs

Intensity I > 0 unless otherwise noted.

(hkl)	d_{hkl}	$n\lambda$	I
$01\bar{1}$	5.31 Å	0.34 Å	
021	4.46	.48	0
$02\bar{1}$	"	.29	0
031	3.65	.29	
$03\bar{1}$	"	.23	
031	"	.39	
$0\bar{7}1$	1.92	.44	
013	1.89	.38	
0.10.1	1.39	.57	0
$0.\bar{1}1.2$	1.18	.46	0
0.12.1	1.16	.49	0
035	1.11	.45	
$0.\bar{1}3.1$	1.08	.38	
0.13.1	"	.42	
$0.\bar{1}3.2$	1.00	.28	0
$0.\bar{1}5.1$	.94	.29	
0.15.1	"	.32	
$0.\bar{1}5.2$	.90	.55	0
0.15.2	"	.41	0

Table III, Continued

(hkl)	d_{hkl}	$n\lambda$	I
0.17.2	0.80 Å	0.31 Å	0
$0.\bar{1}9.1$	.74	.33	
$0.\bar{1}\bar{9}.2$	.73	.35	0
$03\bar{8}$	.71	.26	0
$0.\bar{2}1.2$	.66	.29	0
$0.\bar{2}\bar{3}.2$	.60	.24	0
0.23.3	.59	.37	
$0.\bar{2}\bar{1}.5$	.58	.35	
$0.\bar{2}\bar{5}.3$	.55	.41	
$0.9.\bar{1}\bar{1}$	.49	.34	
0.9.11	"	.28	
105	1.12	.43	0
$10\bar{5}$	"	.54	0
501	1.00	.37	0
$\bar{5}01$	"	.32	0
502	.96	.38	
106	.94	.29	
$10\bar{6}$	"	.39	
$10\bar{6}$	"	.48	
$10\bar{7}$	.73	.27	0
$10\bar{8}$	.71	.30	
702	.70	.32	
702	.70	.36	

Table III, Continued

(hkl)	d_{hkl}	$n\lambda$	I
$\bar{7}02$	0.70 Å	0.33 Å	
$\bar{7}02$	"	.38	
703	.68	.30	0
308	.66	.42	
308	"	.47	
704	.65	.41	
$\bar{9}02$	.55	.25	0
$\bar{9}02$	"	.34	
3.0.10	.54	.32	
3.0.$\bar{1}0$	"	.37	
904	.53	.36	
904	"	.39	
$\bar{9}04$	"	.37	
$\bar{9}04$	"	.41	
230	2.24	.31	
$\bar{3}10$	1.68	.46	0
1.10.0	1.37	.49	0
290	1.34	.31	
1.11.0	1.25	.46	0
$\bar{4}30$	1.23	.44	
1.12.0	1.15	.43	0
1.$\bar{1}2$.0	"	.48	0

Table III, Continued

(hkl)	d_{hkl}	$n\lambda$	I
1.$\bar{1}$3.0	1.07 Å	0.42 Å	0
1.13.0	"	.40	0
1.14.0	1.00	.42	0
1.$\bar{1}$4.0	"	.36	0
1.14.0	"	.38	0
530	.99	.38	0
$\bar{5}$30	"	.47	0
1.15.0	.93	.37	0
1.$\bar{1}$5.0	"	.32	0
1.15.0	"	.36	0
1.16.0	.88	.32	0
1.17.0	.83	.32	0
1.18.0	.78	.26	0
$\bar{7}$30	.72	.25	0
3.25.0	.54	.36	0

8d: $x-\frac{1}{4},y,z-\frac{1}{4}$; $x+\frac{1}{4}$, $\frac{1}{2}-y,\frac{3}{4}-z$; $x-\frac{1}{4},\frac{1}{2}-y,z+\frac{1}{4}$; $x+\frac{1}{4},y,\frac{1}{4}-z$;

$\frac{3}{4}-x,\bar{y},z-\frac{1}{4}$; $\frac{1}{4}-x,\bar{y},\frac{1}{4}-z$; $\frac{1}{2}-x,y+\frac{1}{2},\frac{3}{4}-z$; $\frac{3}{4}-x,y+\frac{1}{2},z+\frac{1}{4}$.

The minimum number of parameters which must be evaluated to determine the atomic positions of the 4 Fe, 8 Cb, and 24 O is seven, and a larger number is necessary if the atoms are to be homogeneously distributed throughout the unit cell. Recourse to the non-rigorous principles developed in recent years for the solution of complex ionic structures is accordingly indicated.

II. The Application of the Coördination Principles, with Closest Packing[7]

Since the crystal radius of Fe^{2+} is 0.75 Å, of Cb^{5+} is 0.70 Å, and of $O^{=}$ is 1.40 Å,[8] it may be assumed that the metal-to-oxygen distances in tantalite are 2.0 ± 0.2 Å. From the univalent crystal radius of Cb^{5+}, a coördination number of six for the ion in oxides has been predicted[9]; and although the univalent crystal radius of Fe^{2+} has not been calculated, its crystal radius suggests that this ion also will coördinate six oxygen ions about it. The octahedra of oxygens will be distorted, but because of the deformability of the iron octahedron, resulting from the large size of

the central ion and from its low valence compared to that of the columbium, the distortion will be left for determination by the intensity data. Union of the octahedra to form the completed structure will be accomplished without the sharing of faces (three oxygens) between columbium octahedra or between columbium and iron octahedra, and the number of shared edges should be small. Lastly, it is expedient to assume that the oxygen framework is derivable by distortion of a close-packed assemblage with the normal to the layers parallel to the b-axis of columbite. The four assumptions - of reasonable metal-to-oxygen distances, of fairly regular octahedra, of limited sharing of oxygens, and of close packing - suffice to define, under the restrictions imposed by the space group and unit cell, a small class of structures from which one may be selected for detailed testing with the observed intensities of reflection.

Arrangements of ions in closest packing have been described [10] in terms of the order of superposition of the three fundamental layers from which all of the infinite number of close-packed structures can be built; namely, A, with an atom at $X = 0$, $Y = 0$ (X,Y,Z being hexagonal coördinates); B, with an atom at $X = 1/3$, $Y = 2/3$; and C, with an atom at $X = 2/3$, $Y = 1/3$. The effective thickness of a layer of oxygen ions is approximately 2.3 Å. If distortion is assumed

to alter the height per layer by a maximum of 15%, the length of the b-axis of columbite then requires that the succession of layers have a periodicity six. Accordingly, the layers may be superposed in the order ABABAB..., giving hexagonal close packing; in the order ABABAC..., giving triple-hexagonal close packing; in the order ABCABC..., giving cubic close packing; in the order ABCACB..., giving double-cubic close packing; and in no other non-equivalent sequence.

The triple-hexagonal close-packed assemblage lacks a diagonal glide plane normal to the layers and containing a two-fold rotation axis parallel to them. The unit with space-group symmetry V_h^{14} therefore cannot be derived from such an oxygen skeleton.[11] The cubic close-packed framework of oxygens with triad axis parallel to b is similarly eliminated.

Normal to the layers of the double-cubic close-packed arrangement there is only one distinct set of glide planes with a diagonal translation, and normal to these planes and to the layers only one distinct set of symmetry planes with a simple glide. The close-packed assemblage can be inserted into a unit with space group V_h^{14} in only one distinct way. The oxygens are in three sets of 8d positions, with parameter values:

$x_1 = 5/6$ $x_2 = 5/6$ $x_3 = 1/2$

$y_1 = 1/12$ $y_2 = 5/12$ $y_3 = 3/4$

$z_1 = 1/8$ $z_2 = 1/8$ $z_3 = 1/8$

If the oxygen ion is assigned the diameter 2.76 Å, the axial lengths are a = 4.78 Å, b = 13.5 Å, c = 5.52 Å; they deviate by 6, 5, and 4%, respectively, from those of the actual structure. This is the arrangement shown in Figure 2. If four iron atoms are inserted into this oxygen framework in the unique positions 4a or 4b, there are no reasonably regular octahedra of oxygen ions about them, and the shortest iron-to-oxygen distance is only 1.4 Å; the unique positions are therefore not available. If, however, they are placed in positions 4c, with u = 3/8, each is surrounded by oxygen atoms at a distance of 1.95 Å, arranged in a regular octahedron, and each octahedron shares two edges with the adjoining ones to form parallel to the a axis strings of the type which were observed in brookite[12](Fig.1). Save for the equivalent parameter value u = -1/8, there is no other value of u which places the iron atoms within reasonably regular octahedra or at distances of the order of 2 Å from the neighboring oxygens. (Small parameter variations, with Δu of the order of 1/8, are of course left to be considered when the structure is tested with the observed intensities of reflection.) Similarly, there are but two

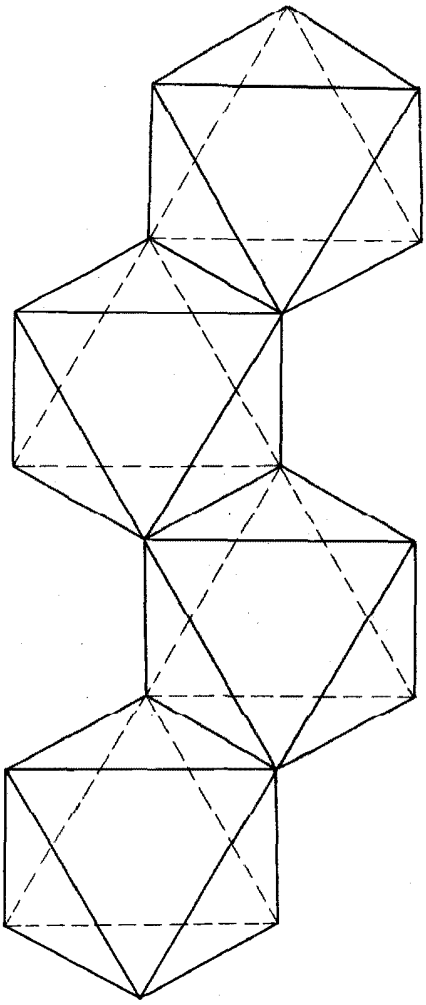

Fig. 1. A string of staggered octahedra.

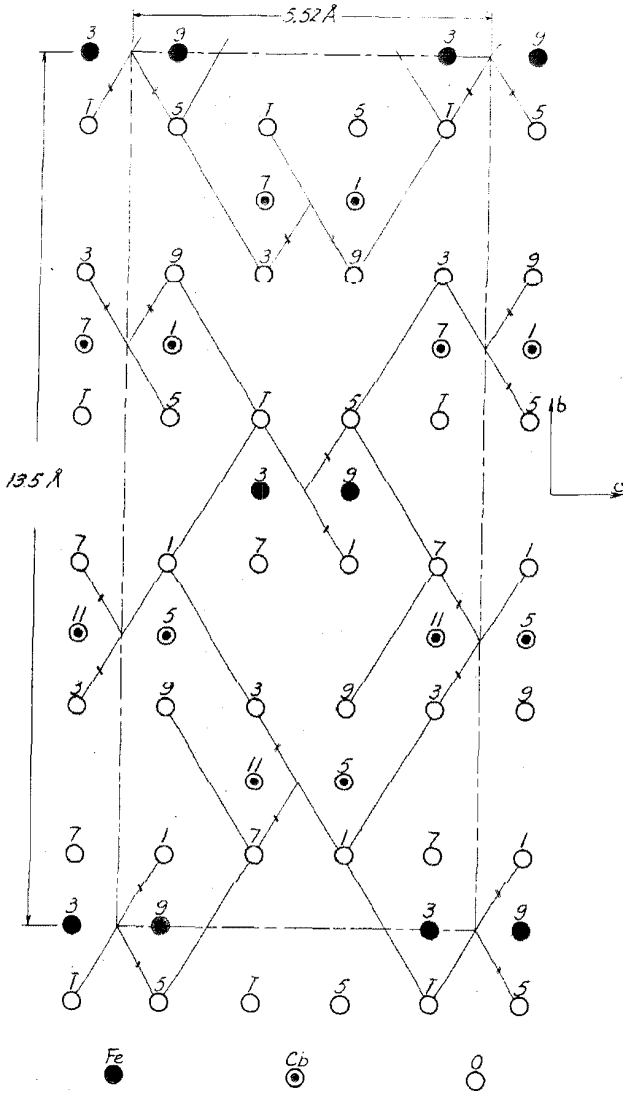

Fig. 2. The projection of (100) of Structure E, undistorted. The edges of the unit cell are outlined, and the uppermost face of each octahedron is indicated. The strings lie normal to the plane of projection; edges shared to form them are marked by double lines. The numeral beside each atom gives its depth in twelfths of a.

sets of positions for the columbium atoms; both place the metals within strings of staggered octahedra, with metal-to-oxygen distances 1.95 Å. If the columbiums are in one of these sets of positions,

$$8d: \quad x = 2/3, \; y = 1/6, \; z = 3/8,$$

each columbium octahedron shares two edges with columbium octahedra of the same string, two edges with an iron octahedron, and two corners with columbium octahedra of an adjacent string. This set of parameters is improbable; it is discarded for this and for another more convincing reason which will appear later.[13] If the second set of available parameter values is chosen,

$$8d: \quad x = 2/3, \; y = 1/6, \; z = 7/8,$$

each columbium string is joined to an adjacent iron string by the sharing of one additional edge per octahedron (the type of linking observed in brookite); and only corners are shared between successive columbium strings. The electrostatic valences of the three groups of oxygens are $1\frac{1}{2}$, 2, and $2\frac{1}{2}$, respectively. Fig. 2 shows this structure, hereafter called Structure E.

The examination of the hexagonal close-packed arrangement (with its hexagonal axis parallel to b) is similar to that of the double-cubic close packing. Only one distinct unit can be derived from it which has the space group V_h^{14} and the basal translations of which approach a and c within 40%. The oxygens are in three sets

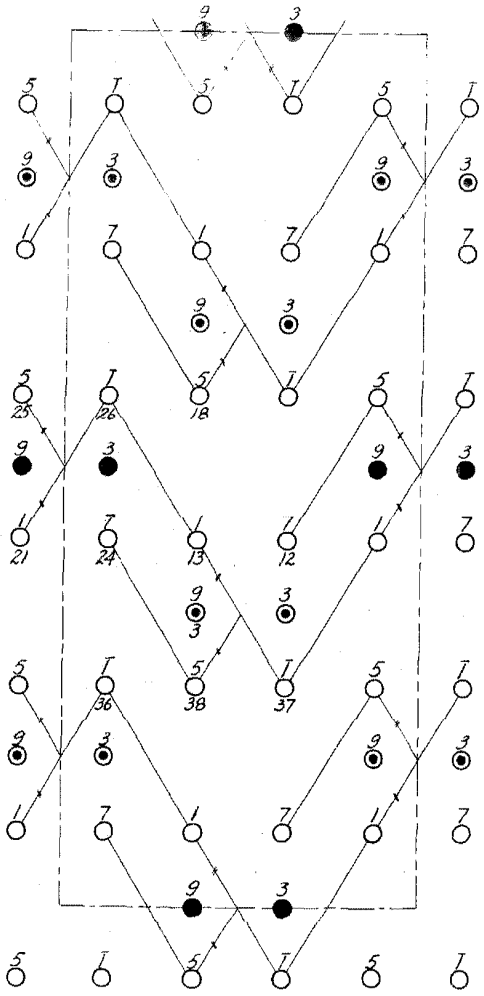

Fig. 3. The projection on (100) of Structure C. See Fig. 2 for explanation of symbols. The lower numeral beside an atom, when two are present, refers to the numbering in Table VI.

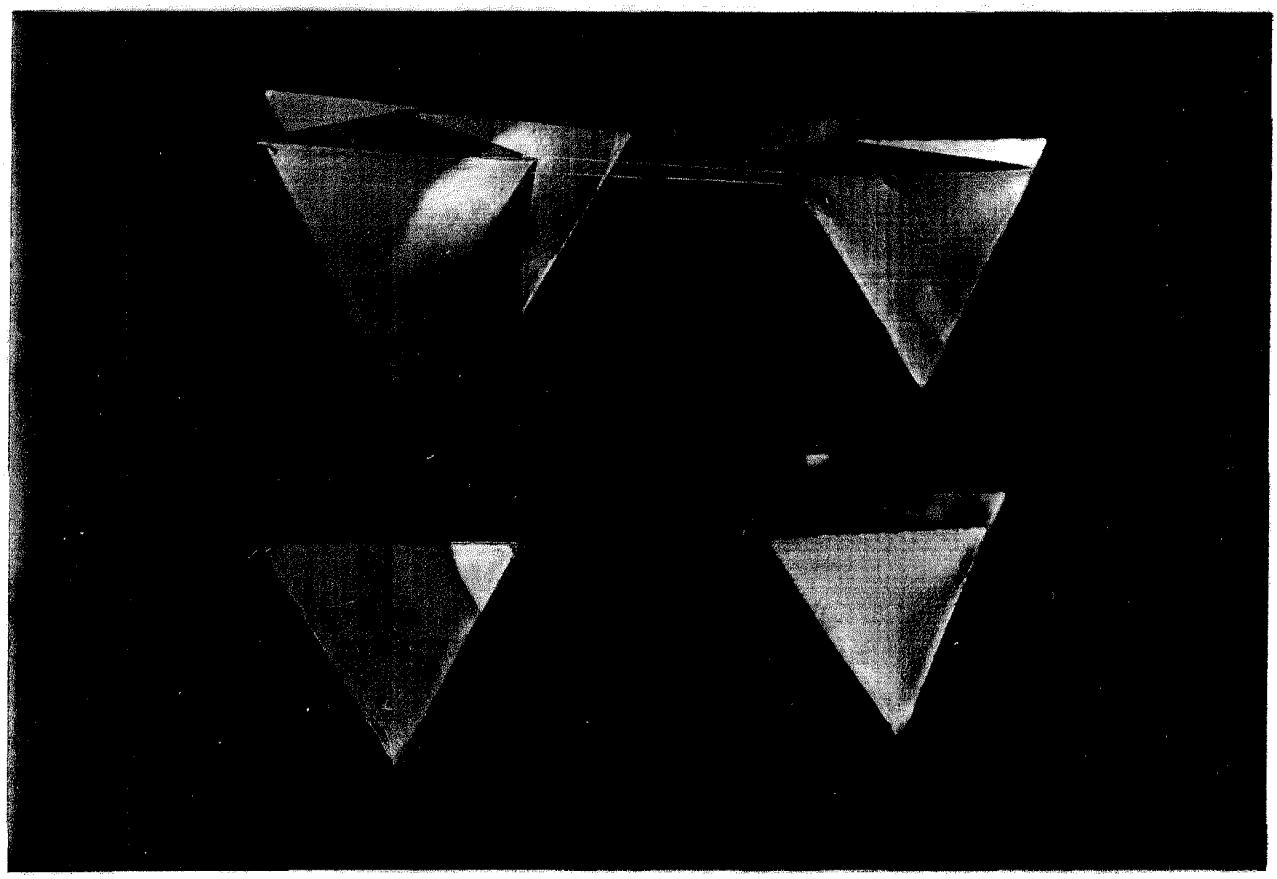

Fig. 4. A model representing half of the unit of structure of columbite, showing the strings of octahedra combined by sharing corners only.

of 8d positions (see Fig. 3); their parameters are:

$x_1 = 1/3$	$x_2 = 1/3$	$x_3 = 1/3$
$y_1 = 1/12$	$y_2 = 5/12$	$y_3 = 3/4$
$z_1 = 1/8$	$z_2 = 1/8$	$z_3 = 1/8$

The iron atoms must lie in positions 4c with u = 5/8. (Setting u = 1/8 produces an equivalent arrangement.) The columbium atoms must be in one of two sets of 8d positions. If they have the parameter values

$$x = 0,\ y = 1/6,\ z = 5/8,$$

each columbium octahedron shares a face with an iron octahedron; this structure disagrees with our original hypotheses. They must then have the positions corresponding to

$$x = 0,\ y = 1/6,\ z = 1/8.$$

The resulting unit, hereafter called Structure C, is shown in Fig. 3, and a model of a portion of it in Fig. 4. It has been found to be the structure of columbite. All of the metal atoms lie within regular octahedra of oxygen atoms. Iron octahedra share two edges each to form strings parallel to the a axis, and columbium octahedra do likewise; each string of staggered octahedra is joined to two adjacent strings by the sharing of corners only. The electrostatic valences of the three groups of oxygens are 2, $1\frac{1}{2}$, and $2\frac{1}{2}$, respectively. In short, Structure C differs from Structure E only in the sharing of corners instead of edges between

iron and columbium octahedra. The principles which have been adopted indicate that Structure C is slightly more probable than the other.

A choice between Structures C and E is easily made by comparison of the observed intensities of reflection from (200) and (400) with intensities calculated from each of the two structures, which differ only in the distributions parallel to a. (It is assumed that the relative intensities of the lower orders will not be largely affected by distortion.) Oscillation photographs show a normal decline in intensity for even orders from (100); i.e., they suggest approximate equality of the structure factors for these orders. The calculated structure factors are:

Structure E: $S_{200} = -2\,Fe + 2\,Cb - 4\,O.$

$S_{400} = 2\,Fe - 2\,Cb.$

Structure C: $S_{200} = -2\,Fe - 4\,Cb + 12\,O.$

$S_{400} = 2\,Fe + 4\,Cb - 12\,O.$

Structure C is accordingly selected as suitable for detailed comparison with the intensity data.

III. Testing the Structure with the Estimated Intensities of Reflection

Oscillation photographs were prepared with the

molybdenum Kα lines, isolated by a zirconia filter, reflected from the ground pinacoids of the crystal, a crystallographic axis being made the axis of rotation. Reflections employed in the limitation of the parameters were identified by measurement of latitude and azimuth on the film; for a control, the spheres of reflection in the reciprocal lattice were constructed. As an added precaution against the confusion of prisms and pyramids, each oscillation photograph was repeated with the crystal rotated a few degrees about the normal to the reflecting face; when a, say, was the axis of rotation and (010) the reflecting face, this displaced vertically reflections from forms with $l \neq 0$. Because of the length of the b-axis, reflections from planes with k = 0 and with k = 1 were superposed, save when b was the axis of rotation; photographs from (100) with c the axis of rotation, and from (001) with a the axis of rotation were therefore not used in the testing of the structure. All reflections from planes whose traces in the reflecting face were not normal to the axis of rotation were likewise ignored, because of the probability that the intensities of such reflections are strongly influenced by absorption.

The relative intensities of useful lines on the various photographs were estimated by visual comparison with a scale bearing eighteen lines of darkenings corresponding to various values of the product X-ray intensity

times time from 0.25 to 30.

The origin of the unit cell of columbite has been chosen at a center of symmetry. In this case, neglecting extinction, and with the oscillating crystal method as described, a quantity proportional to the integrated intensity of reflection from a plane (hkl) is ωA^2, where

$$A = \sum_{i,j}' A_i \cos(h\xi_{ij} + k\eta_{ij} + l\zeta_{ij}),$$

$$1/\omega = \left[1 - (u\lambda/d\sin 2\vartheta)^2\right]^{1/2},$$

$$A_i = \left(\frac{1 + \cos^2 2\vartheta}{2 \sin 2\vartheta}\right)^{1/2} F_i.$$

The factor $1/\omega$ is a correction for the varying specific times of illumination of planes inclined to the axis of rotation; u is the index (i.e., h, k, or l) corresponding to the axis of rotation, and d is the unit translation along that axis.[14] The triple $(\xi_{ij}, \eta_{ij}, \zeta_{ij})$ are the coördinates of the j^{th} atom of the i^{th} species referred to the axes of the unit cell, and the summation is over a certain half of the atoms of each kind in the unit cell; namely, over that half from which the others are obtainable by inversion through the origin. F_i denotes the usual F factor for the i^{th} kind of atom. The quantity ωA^2, and less accurately A, must approximately parallel the estimated relative intensities of reflection on any one

photograph.

The F curves employed for iron and oxygen are taken from the tabulation by Bragg and West.[15] The F curve for columbium is calculated from Thomas' atomic model according to the method given by the same authors, and is corrected for the heat motion by an arbitrarily chosen factor less than unity and decreasing with increase of ϑ; the resulting F values are given in Table IV. Although molybdenum Kα radiation ($\nu/R = 1287$) is softer than the K edge of columbium ($\nu/R = 1401$) and near it, no correction for the change of the amplitude-ratio in a region of anomalous dispersion is necessary.[16] The effect of the presence of tantalum in the observed ratio atoms Cb: atoms Ta = 89:11 was estimated from the F curve for tantalum according to the Thomas model to be equivalent to an increase of about 10% in the F curve employed for columbium. Since this effect is opposite to that of the anomalous dispersion, and in view of the inexactness of the intensity estimates as well as of the F curves themselves, the presence of tantalum was likewise neglected.

The parameters of the metal atoms along each axis were fixed successively. A values of high orders from (010) were first examined as functions of the single parameter y_{Cb} on the interval $0 \leq y_{Cb} \leq 0.25$. Allowance was made for the maximum possible contribution to any A

Table IV

F values for columbium

$\frac{\sin\vartheta}{\lambda}$	F
0.0	41.
.1	35.5
.2	30.0
.3	24.8
.4	21.3
.5	18.7
.6	16.5
.8	12.9
1.0	10.4
1.2	8.6

from the oxygens; for the higher orders this maximum (equal to 12 A_O) is conveniently small. Observed inequalities of various lines (Table V, Photographs C and E) sufficed to fix $0.159 \leq y_{Cb} \leq 0.170$, and the most satisfactory agreement was obtained with $y_{Cb} = 0.163$. The oxygen parameters y_1, y_2, y_3 were then chosen to give agreement for all orders from (010), especially for those for which $A_{Cb} + A_{Fe}$ is small. With y_{Cb} evaluated, the A values of high-order reflections of form (hk0) (Table V, Photograph C) were treated similarly as functions of the single parameter x_{Cb}, with $-0.25 \leq x_{Cb} \leq 0.25$; only on the subinterval $-0.04 \leq x_{Cb} \leq 0.04$ did the A curves duplicate the observed order of intensities. To explain simply the facts that the intensities of high-order reflections (hk0) appear to be independent of h and to vanish when k is odd, x_{Cb} was made zero.[17] The oxygen parameters x_1, x_2, x_3 were then chosen with regard to the intensities of lower orders. In like fashion, z_{Cb} and u were limited by large-angle reflections of form (0kℓ) (Table V, Photograph E). They were varied over the intervals $0 \leq z_{Cb} \leq 0.25$, $0.50 \leq u \leq 0.75$. The use of inequalities alone requires $0.12 \leq z_{Cb} \leq 0.22$, and $u < 0.70$; satisfactory agreement is obtained only within a much smaller region.

The following set of parameters was found to give

the best agreement with all of the 127 prisms and pinacoids identified on the oscillation photographs:

$x_{Cb} = 0.000$	$x_1 = 0.333$	$x_2 = 0.333$	$x_3 = 0.320$
$y_{Cb} = 0.163$	$y_1 = 0.090$	$y_2 = 0.410$	$y_3 = 0.750$
$z_{Cb} = 0.075$	$z_1 = 0.155$	$z_2 = 0.150$	$z_3 = 0.170$

$$u = 0.600$$

Comparison of these parameter values with those for the undistorted Structure C shows that distortion has produced only slight relative shifts along the a and b axes, and a maximum change of 0.05 parallel to the c axis.

Table V gives the values of ωA^2 calculated with the corresponding atomic positions. If any one of the four metal parameters is altered by as much as 0.005, the qualitative agreement is markedly poorer. The oxygen parameters along b seem to be fixed within the same limits. Those along a and c, however, are determined by the intensities at best to a few hundredths; they are fixed at the values given by the assumption that the distance from a columbium atom to an oxygen is 2.0 ± 0.1 Å.

IV. The Discussion of the Structure

Fig. 4 is a photograph of a model representing one-half of the unit of structure of columbite. Any one string contains only iron or only columbium ions at the

TABLE V

Photograph A: X-rays incident on (100), b-axis vertical; oscillation 0-45°; 42 kv. peak; 220 milliampere hours

Equator			2nd Layer Line			3rd Layer Line			4th Layer Line			6th Layer Line		
(hkl)	I	$\omega A^2 .10^{-4}$	(hkl)	I	$\omega A^2 .10^{-4}$	(hkl)	I	$\omega A^2 .10^{-4}$	(hkl)	I	$\omega A^2 .10^{-4}$	(hkl)	I	$\omega A^2 .10^{-4}$
200	17.	13.9*	220	.01	.24*	230	8.6	2.9*	240	.5	.93*			
400	7.5	3.3				430	.5	.19	440	.25	.13	460	7.0	4.0
600	2.0	1.93				630	.00	.00				660	.6	.91
800	.20	.53										860	.2	.59

TABLE V

Photograph B: X-ray beam incident on (010), a-axis vertical; oscillation 0-30°; 40 kv. peak; 75 milliampere-hours

Equator			2nd Layer Line		
(hkl)	I	$\omega A^2 .10^{-4}$	(hkl)	I	$\omega A^2 .10^{-4}$
040	1.5	2.5*	240	.35	1.3*
			250	v v w	.02*
060	5.5	7.4*	260	10	23.*
			270	.00	.04*
080	v w	.03*	280	.00	.03*
			290	.3	.39*
0.10.0	.35	.45*	2.10.0	.6	.67*
			2.11.0	.00	.01*
0.12.0	~5.	4.1	2.12.0	2.5	3.1*
			2.13.0	.00	.01*
0.14.0	.00	.00	2.14.0	v w	.03*
			2.15.0	v v w	.04*
0.16.0	.2	.30	2.16.0	.2	.31*
			2.17.0	.00	.00
0.18.0	.5	.72	2.18.0	.8	1.00

TABLE V

Photograph C: X-ray beam incident on (010), a-axis vertical; oscillation 20-50°; 40 kv. peak; 225 milliampere-hours

Equator			2nd Layer Line			4th Layer Line		
(hkl)	I	$\omega A^2 .10^{-4}$	(hkl)	I	$\omega A^2 .10^{-4}$	(hkl)	I	$\omega A^2 .10^{-4}$
			2.15.0	∽.1	.03			
0.16.0	1.0	.30	2.16.0	.6	.21	4.16.0	.35	.14
			2.17.0	.00	.00	4.17.0	.00	.00
0.18.0	1.7	.72	2.18.0	2.5	1.00	4.18.0	1.6	.78
			2.19.0	.00	.00	4.19.0	.00	.00
0.20.0	.2	.04	2.20.0	v v w	.01	4.20.0	v v w	.12
			2.21.0	.00	.00	4.21.0	.00	.00
0.22.0	.35	.13	2.22.0	.25	.13	4.22.0	∽.2	.11
			2.23.0	.00	.00	4.23.0	.00	.00
0.24.0	.8	.37	2.24.0	.5	.31	4.24.0	.35	.30
			2.25.0	.00	.00			
0.26.0	∽.1	.02	2.26.0	∽.1	.03			

TABLE V

Photograph D: X-ray beam incident on (010); c-axis vertical; oscillation 0-30°; 40 kv. peak; 75 milliampere hours

Equator			1st Layer Line			2nd Layer Line			3rd Layer Line		
(hkl)	I	$\omega A^2.10^{-4}$	(hkl)	I	$\omega A^2.10^{-4}$	(hkl)	I	$\omega A^2.10^{-4}$	(hkl)	I	$\omega A^2.10^{-4}$
020	1.4 ?	2.4*	031	12.	13.5*						
040	2.2	2.5*	051	.00	.00*						
060	8.	7.4*	071	.2	.10*	062	5.	4.1*			
080	∽.05	.03*	091	2.	1.4	082	.00	.00*			
0.10.0	.5	.45*	0.11.1	.00	.00	0.10.2	.5	.45*	093	∽2.5	6.6*
0.12.0	4.5	4.1	0.13.1	.00	.01	0.12.2	1.5	.43	0.11.3	.00	.00
0.14.0	.00	.00	0.15.1	.5	.41	0.14.2	.00	.01	0.13.3	.2	.28
0.16.0	.2	.30	0.17.1	.00	.01	0.16.2	∽.05	.11	0.15.3	1.5	1.37
0.18.0	.5	.72	0.19.1	v v w	.02	0.18.2	.25	.31			

TABLE V

Photograph E: X-rays incident on (010); c-axis vertical; oscillation 20-50°; 40 kv. peak; 250 milliampere hours

Equator			1st Layer Line			2nd Layer Line			3rd Layer Line		
(hkl)	I	$\omega A^2 .10^{-4}$	(hkl)	I	$\omega A^2 .10^{-4}$	(hkl)	I	$\omega A^2 .10^{-4}$	(hkl)	I	$\omega A^2 .10^{-4}$
									0.13.3	1.	.28
						0.14.2	∽.05	.01			
			0.15.1	2.5	.41				0.15.3	6.	1.37
0.16.0	1.2	.30				0.16.2	.5	.11			
			0.17.1	.00	.01				0.17.3	∽.15	.01
0.18.0	2.3	.72				0.18.2	1.	.31			
			0.19.1	.2	.02				0.19.3	.5	.15
0.20.0	.25	.04				0.20.2	∽.01	.00			
			0.21.1	.2	.13				0.21.3	.8	.43
0.22.0	.5	.13				0.22.2	.2	.06			
			0.23.1	∽.1	.01				0.23.3	.2	.02
0.24.0	1.0	.37				0.24.2	.25	.08			
			0.25.1	.00	.01				0.25.3	.2	.08
0.26.0	∽.1	.02				0.26.2	∽.1	.01			
			0.27.1	.2	.06						
0.28.0	.2	.08									

TABLE V

Photograph F: X-rays incident on (001); b-axis vertical; oscillation 0-30°; 40 kv. peak; 190 milliampere hours
(The estimation of the intensity of 0.0.10 is obtained from photographs at larger angles.)

Equator			1st Layer Line			2nd Layer Line			3rd Layer Line			4th Layer Line		
(hkl)	I	$\omega A^2.10^{-4}$	(hkl)	I	$\omega A^2.10^{-4}$	(hkl)	I	$\omega A^2.10^{-4}$	(hkl)	I	$\omega A^2.10^{-4}$	(hkl)	I	$\omega A^2.10^{-4}$
002	15-30	3.1*	011	∽1.	.49*	022	.8	.27*	031	15-30	17.*	042	1.2	1.09*
004	8.	2.0	013	.5	.37*	024	.00	.04	033	15-30	13.*	044	.00	.00
006	5.	1.12	015	.35	.25	026	v v w	.04	035	6.	.88	046	∽.1	.10
008	1.	.25	017	v v w	.03	028	v v w	.12	037	v v w	.01			
0.0.10	.00	.01												

5th Layer Line			6th Layer Line			7th Layer Line			8th Layer Line			9th Layer Line		
053	∽.2	.09*	062	6.	9.7*	073	1.5	.49	084	v v w	.04	095	5.	.69
055	∽.2	.21*	064	v v w	.27	075	.6	.31						
057	.00	.02	066	5.	$2.3\overset{o}{\underset{\wedge}{\phi}}$									

center of its octahedra; one layer of iron strings follows two layers of columbium strings. Three metal ions are about each oxygen ion. The interatomic distances are shown in Table VI. Distortion from close packing subsequent to the insertion of the large coördinating ions has resulted in an expansion of all octahedra, the mean increase in the edges of the columbium octahedra from the originally assumed length of 2.76 Å being 4% and of the iron octahedra 8%. Although no use was made of the principle that edges shared between octahedra should be most shortened, the rule is obeyed by the columbium octahedra; since it appears to be invalid for the iron octahedra, the $Fe^{2+} - Fe^{2+}$ repulsion is unimportant compared to other interionic forces.

While Structure C is in accord with most of the principles that have been suggested for ionic structures, the deviation of the electrostatic valences of the oxygens from the value two is large. Qualitatively, the strength of a bond as defined by Pauling[7] (i.e., the positive potential at the location of the anion arising from a neighboring cation) should be considered to increase with decreasing anion-cation distance, and the columbium-oxygen distances should be observed to decrease in the order $Cb-O_3$, $Cb-O_1$, $Cb-O_2$. In agreement with this prediction, what seems to be the most satisfactory agreement between calculated and observed intensities appears when the distance $Cb-O_2$ is shorter by

Table VI

Interatomic distances in columbite

Distances equivalent by symmetry are bracketed; shared edges are marked by asterisks.

Iron octahedron			Columbium octahedron		
		Elec. valence of oxygen			Elec. valence of oxygen
Fe_2-O_{13}	2.12 Å	2	Cb_3-O_{24}	1.86 Å	1½
Fe_2-O_{18}			Cb_3-O_{13}	2.04	2
Fe_2-O_{21}	2.10	1½	Cb_3-O_{12}	2.05	2
Fe_2-O_{25}			Cb_3-O_{36}	2.09	2½
Fe_2-O_{24}	2.14	1½	Cb_3-O_{38}	2.11	2½
Fe_2-O_{26}			Cb_3-O_{37}	2.12	2½
O_{24}-O_{21}	2.79		O_{12}-O_{38}	2.61*	
O_{25}-O_{26}			O_{13}-O_{37}		
O_{13}-O_{21}	2.89		O_{37}-O_{38}	2.70	
O_{18}-O_{25}			O_{12}-O_{13}	2.76	
O_{24}-O_{25}	2.93*		O_{12}-O_{24}	2.84	
O_{21}-O_{26}			O_{36}-O_{37}	2.86	
O_{13}-O_{18}	3.07		O_{12}-O_{37}	2.88	
O_{21}-O_{25}	3.07		O_{24}-O_{36}	2.88	
O_{13}-O_{24}	3.08		O_{24}-O_{38}	3.02	
O_{18}-O_{26}			O_{13}-O_{36}	3.04	
O_{13}-O_{26}	3.22		O_{13}-O_{24}	3.08	
O_{18}-O_{24}			O_{36}-O_{38}	3.20	
Average	3.00		Average	2.87	

approximately 0.1 Å than any other columbium-oxygen distance. That $Cb\text{-}O_3$ is larger than $Cb\text{-}O_1$ is uncertain.

Brögger and Prior have observed a close crystallographic relationship between columbite and brookite.[18] It is now seen that the structure of columbite also is similar to the structure of brookite; the two are differentiated by the manner in which successive strings are connected, and consequently by the number of edges shared per octahedron. It is satisfactory, but of doubtful significance, to find that with the replacement of quadrivalent cations by bivalent and quinquevalent ones, that is, with the change from the molecule Ti_3O_6 to the molecule $FeCb_2O_6$, the number of shared edges per octahedron in otherwise similar structures decreases from three to two.

The undistorted Structure C is exactly the Structure A which was built up in the study of brookite,[19] except for the tripling of the unit caused by the presence of the two kinds of metal atoms. The two oscillation photographs shown in Figs. 5 and 6 evidence strikingly the pseudo-unit, with a b axis one-third that of columbite, and with the same distribution of symmetry elements. They led early in the present study to the prediction[20] that the columbite unit would prove to be a triple of the unit of Structure A, and to the rapid derivation by the coördination

Fig. 5. Photograph D of Table V.

Fig. 6. Photograph F of Table V.

theory alone, with no assumption of close packing, of both Structures C and E. Only when it was proved that no structure of the proper symmetry containing strings of octahedra could satisfy the electrostatic principle exactly was the hypothesis of close packing substituted for the hypothesis of strings of octahedra. It has been seen that it was at least impracticable to apply the later hypothesis in a form more lenient than the earlier one.

Summary

A crystal of columbite-tantalite, $(Fe,Mn)(Cb,Ta)_2O_6$, containing principally columbite was found by the use of Laue and oscillation photographs to have an orthorhombic unit of structure of dimensions $a = 5.082$ Å, $b = 14.238$ Å, $c = 5.730$ Å, containing four molecules. The space group is V_h^{14}. By the use of the coördination theory and of close packing, a number of possible structures were devised, and one was shown to have the observed unit and symmetry, and to explain the intensities of reflections on oscillation photographs. Its structural element is an octahedron of oxygen ions about a metal ion; each octahedron shares two edges with adjoining ones to form

strings of either columbium octahedra alone or of iron octahedra alone, and the strings are united by the sharing of corners. A diagram of the structure is shown in Fig. 3, a model in Fig. 4.

References

1. The crystallography and chemistry of the system are discussed in Dana, Mineralogy, 731-736 (6th ed., New York, 1920); P. Niggli and K. Faesy, Z. Krist., 61, 349-354 (1925); Mellor, Treatise on Inorg. and Theoret. Chem., IX, 906-910 (New York, 1929); etc.

2. This crystal was furnished through the kindness of Professor J.R.Oppenheimer.

3. E.S.Dana, Z. Krist., 12, 271 (1887). Dana's specimen (from Standish, Me.) contained 68.99% Cb_2O_5, 9.22% Ta_2O_5; had a density of 5.65. Within our limits of error, the composition and density are the same as those of the crystal used here. The axial ratio is further not very sensitive to changes in composition.

It may be noted that the axial ratio given by Schrauf corresponds to the X-ray unit, save for the interchange of a and c.

4. Mellor, l.c., p. 908.

5. Space group criteria are given by Wyckoff, Z. Krist., 61, 431-443 (1925); C. Hermann, ibid., 68, 265-270 (1928); etc.

6. R.W.G.Wyckoff, "The Analytical Expression of the Results of the Theory of Space Groups," Publ. Carnegie Institution, No. 318 (1922). For convenience in the calculation of structure factors, the origin of the coördinate system used above has been transferred to a center of symmetry, $(\frac{1}{4},0,\frac{1}{4})$ referred to Wyckoff's origin.

7. Linus Pauling, J.Am.Chem.Soc., 51, 1010-1026 (1929). Concerning close packing, see W.L.Bragg and G.B.Brown., P.R.S., A 110, 34 (1926); W.L.Bragg and J. West, ibid., A 114, 450 (1927).

8. Linus Pauling, J.Am.Chem.Soc., 49, pp. 771 and 780 (1927).

9. Pauling, reference 7, p. 1016.

10. Pauling, reference 7, p. 1022.

11. A convenient description of the symmetry of the

symmetry of the columbite unit is contained in the symbol for Vh^{14} according to Hermann (l.c.); it is $D_{2h}p\nu\gamma\alpha$, with the axes of the present paper.

12. Linus Pauling and J.H.Sturdivant, Z. Krist., 68, 239-256 (1928).

13. Comparison of the columbium parameters just given with those for Structure E below shows that the intensities of reflection from the two structures are the same for planes with ℓ even. Hence the argument from intensities used at the end of this section to eliminate Structure E also eliminates the arrangement just described. It may also be mentioned that the electrostatic valences of the oxygens in the structure are very unsatisfactory, being $2\frac{1}{2}$, $2\frac{1}{3}$, and $1\frac{1}{6}$.

14. H. Ott, Z. Physik, 22, 201 (1924).

15. Z. Krist., 69, 139 (1928).

16. From an approximate formula given by Waller (Z. Physik, 51, 224, 1928) the corrected amplitude factor F' is found to be F - 2.8. That the magnitude of the effect is small is confirmed by recent measurements of Wyckoff (Phys. Rev., 35, 215, 1930).

17. Since A_O is small, one has for these reflections:

$$A = 4\, A_{Cb} \cos\left[h(x_{Cb} + \tfrac{1}{4})\right] \cos k y_{Cb} + (-1)^{h/2}\, 2\, A_{Fe}$$

$$A = -4\, A_{Cb} \sin\left[h(x_{Cb} + \tfrac{1}{4})\right] \sin k y_{Cb}$$

for k even; for k odd;

and h is necessarily even.

18. G.T.Prior, Mineral.Mag., 13, 217 (1903); W.C. Brögger, Min. Südnorw. Granitpeg., 71 (1906).

19. Pauling and Sturdivant, l.c., pp. 248-249.

20. This conclusion was first drawn by Professor Pauling.